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Groundwater-derived nutrient and trace element transport to a nearshore Kona coral ecosystem: Experimental mixing model results

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ABSTRACT

Study region: The groundwater influenced coastal waters along the arid Kona coast ofthe Big Island, Hawai'i.
Study focus: A salinity-and phase partitioning-based mixing experiment was constructed using contrasting groundwater endmembers along the arid Konacoast of the Big Island, Hawai'i and local open seawater to better understand biogeochemical and physicochemical processes that influence the fate of submarine groundwater discharge (SGD)-derived nutrients and trace elements.
New Hydrological Insights for the Region: Treated wastewater effluent was the main source for nutrient enrichment downstream at the Honokōhau Harbor site. Conservative mixing for some constituents, such as nitrate + nitrite, illustrate the effectiveness of physical mixing to maintain oceanic concentrations in the colloid (0.02–0.45 μm) and truly dissolved (<0.02 μm) forms. In contrast, the nonconservative behavior of phosphate highlights the importance of surface complexation reactions that can lead to higher concentrations based on conservative mixing alone. Results from this physiochemical mixing experiment demonstrate how relative availability of P can shift with adsorption behavior, affecting the mobility of phosphate in the environment. With a proposed 8-hectare wastewater treatment facility (WWTF) to be constructed upslope of the Kaloko-Honokōhau National Historical Park (NHP), treated effluent is projected to add additional nutrients. Combined with high permeability, rapid discharge, and increased nutrient loading SGD will likely continue to serve as a persistent source of nutrients and potential contaminant to coral ecosystems.

1. Introduction

Along the arid west coast of the island of Hawai'i submarine groundwater discharge (SGD) is the dominant waterborne transport vector for nutrients and trace elements to the coastal ocean (e.g., Bienfang, 1980; Johnson et al., 2008; Parsons et al., 2008; Street et al., 2008; Peterson et al., 2009; Knee et al., 2010). Chemical export of trace elements is an

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important source to the coastal ocean (Shaw et al., 1998; Basu et al., 2001; Moore et al., 2006; Beck et al., 2007; Bone et al., 2007; Moore, 2010; Santos et al., 2011; Beck and Cochran, 2013; Gonneea et al., 2013) suggesting that "subterranean estuaries" alter nearshore trace element concentrations (Moore, 1996; Santos et al., 2008; Swarzenski and Izbicki, 2009). As a result, discharge of groundwater can impact marine biotic communities by delivering heightened nutrient and trace metal loads that may lead to eutrophication, harmful algal blooms (Anderson et al., 2002), decreased coral abundance and diversity, and increased macroalgal abundance (Fabricius, 2005; Lapointe et al., 2005). In particular, eutrophication caused by nitrogen and phosphorous pollution from land-based sources (e.g., septic leachate, fertilizers), can alter ecosystem function and structure by shifting reefs dominated by corals to algae (Howarth et al., 2000; Andrefouet et al., 2002; Hughes et al., 2007), and increase vulnerability of reefs to coral disease (Bruno et al., 2003; Redding et al., 2013). Therefore, coral reefs directly influenced by SGD are particularly sensitive to land-based activities that can alter groundwater quantity and quality.

The coral reef complex of Honokōhau Bay within Kaloko-Honokōhau National Historical Park (NHP) on the central, leeward coast of Hawai'i provides critical structure (e.g., habitat) for the area's coastal ecosystems. Freshened surface water plumes derived from SGD are prevalent in most areas of the Park within 5-m water depth (Johnson et al., 2008). The influence of SGD in this region was also noted by Parsons et al. (2008) reporting salinities at nearshore reef sites commonly below open ocean values. Elevated nutrient loads observed in coastal groundwater have been attributed to recent land-use changes upslope (e.g., residential subdivisions, golf courses, unsewered suburban and commercial developments, agriculture) as well as the establishment of the Kealakehe Wastewater Treatment Facility (WWTF) (Johnson et al., 2008; Knee et al., 2010; Hunt, 2014). The WWTF discharges effluent into an excavated pit approximately 1 km up gradient from the Honokōhau Harbor at a rate of 4921– 6435 m^3 day^{-1} (Parsons et al., 2008), acting as a point-source for nutrients to the oligotrophic seawater of this region.

The primary aim of this process-level study was to investigate the delivery and transformations of trace elements and nutrients, including the role of colloids in nutrient and metal fluctuations in a subterranean estuary by conducting a series of mixing experiments using two contrasting groundwater endmembers collected from the Kona coast. This experimental mixing approach cannot account for the full spectrum of conditions within a subterranean estuary (e.g., redox conditions, physicochemical properties of the aquifer substrate, and spatial or temporal changes in solution composition within the aquifer) however, results from the mixing model can provide insight on fundamental reactions inherent to the FW-SW mixing zone. For example, along an estuarine salinity gradient, surface complexation models (SCMs) predict that phosphate will desorbs from metal oxyhydroxides as pH increases (e.g., Gao and Mucci, 2001; Gao and Mucci, 2003). Determining the patterns and processes that influence the fate of SGD mixing with nearshore waters is important for effective management of coastal resources where population growth and resulting land development projects may lead to increased stressors to nearshore coral ecosystems on the island of Hawai'i.

2. Methods

2.1. Study site

The island of Hawai'i is the largest of the Hawaiian Islands and lies between 154°48′W and 156°04′W and between latitude 18°54′N and 20°17′N (Fig. 1). The island is composed of five shield volcanoes: Kohala, Mauna Kea, Hualālai, Mauna Loa, and Kīlauea (Langenheim and Clague, 2015; Clague, 1987). The study site is on the Kona Coast on the leeward, west side, bounded on the east by the south-southeast rift zone of Hualālai Volcano and the southwest rift zone of Mauna Loa Volcano, and on the west and south by the Pacific Ocean. The upland area of the of Kaloko-Honokōhau NHP region is composed of three Holocene basalt flows that originated from the Hualālai Volcano (altitude of 2.5 km) and range in age from 10 ka to 1.5 ka (Wolfe and Morris, 1996). The Hualālai volcanics are dominated by alkali basalt with tholeiitic basalt present in submarine samples from dredges (Clague, 1987; Langenheim and Clague, 2015). Thin basalt flows, ranging in thickness from less than a meter to several meters, form aquifers characterized by thin freshwater lenses with high permeability and rapid discharge, with the best developed aquifers in volcanic rocks that formed during the main shield volcano building stage (Gingerich and Oki, 2000). Groundwater flows rapidly from the mountains to the sea, with recharge occurring through infiltration, primarily via precipitation, and inflow from higher groundwater systems (Oki, 1999; Bauer, 2003). Sources of freshwater include recharge up gradient, infiltration of rainfall and fog drip, and irrigation water. The area of highest recharge is at altitudes greater than 600 m. Rainfall is less than 64 cm $year^{-1}$ on the coast but over 250 cm $year^{-1}$ on the mountain slope (Giambelluca et al., 2013). The development of soil is minimal due to the young age of the basalt and low rainfall, therefore rainfall percolates downward, contributing to groundwater rather than overland flow. Hydraulic conductivity within the Park was estimated at 2.3 km day^{-1} and between 0.15 to 10 km day^{-1} north of the Park (Oki, 1999). Groundwater in the Kona area is characterized by a coastal unconfined groundwater system in the form of a freshwater lens, as water impounded to high levels within the inland part of the aquifer with lower overall permeability, and as a coastal confined-groundwater system beneath the coastal freshwater-lens system (Oki et al., 1999; Tillman et al., 2014). Permeability is high within the coastal aquifer and is enhanced by the presence of lava tubes.

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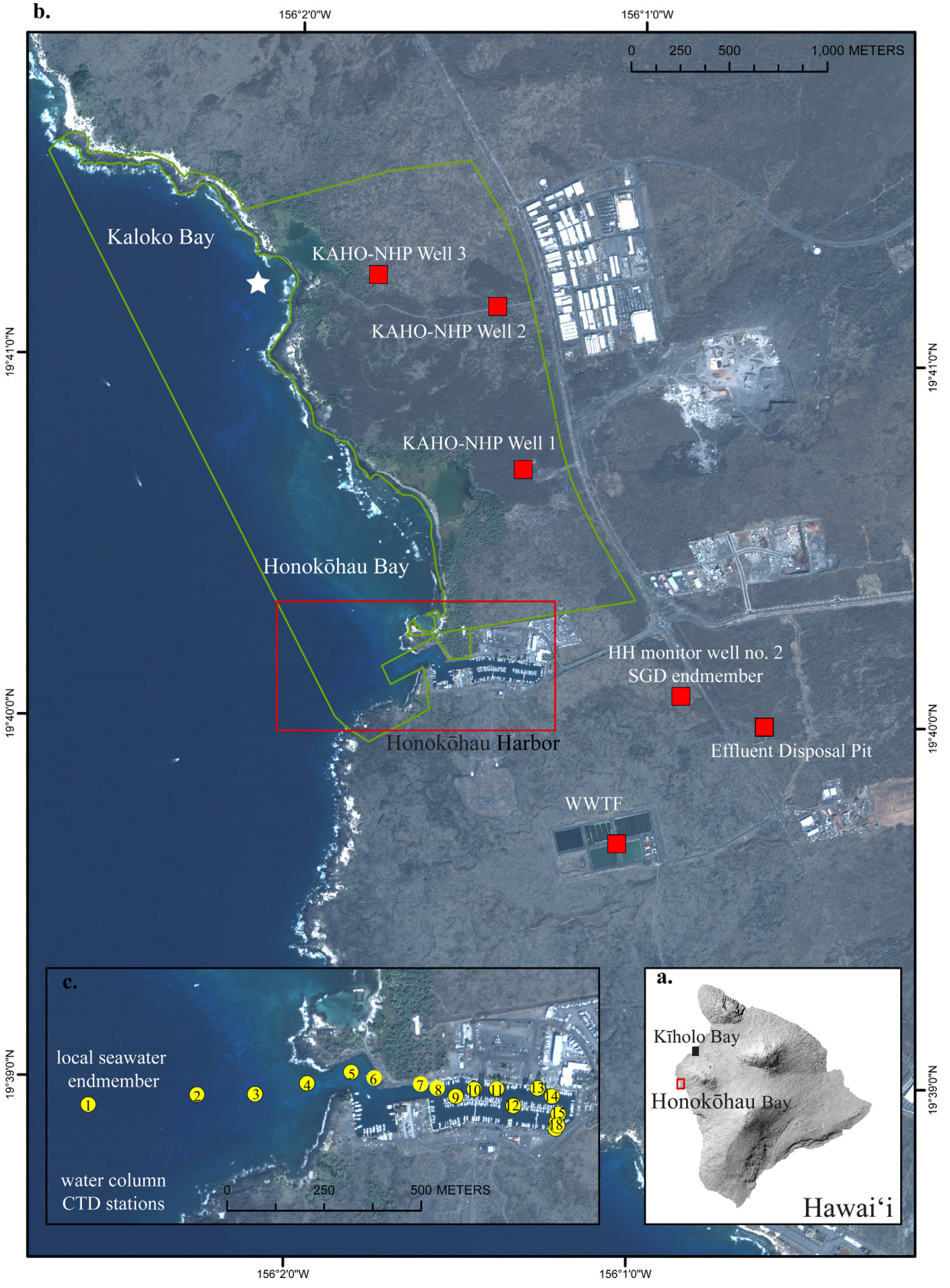

Fig. 1. (a) Map of the Big Island of Hawai'i indicating locations for groundwater sampling sites along the Kona coast including Kīholo Bay,

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Table 1
Sampling sites for groundwater and surface seawater from Kona, Hawai'i and in-situ water properties measured from an YSI multi-sensor probe.

Sample site	Date of collection	State ID	Lat.	Long.	Salinity	Temp. (°C)	pH	DO%	DO mg L^{-1}
HH monitor well no. 2	10/27/12	n/a	19.6679	−156.0144	5.70	23.10	6.9	31.9	2.7
Lava tube, Kiholo Bay	10/28/12	n/a	19.8540	−155.9231	2.08	22.26	7.7	93.8	8.1
KAHO-NHP well 1	10/29/12	4161-01	19.6872	−156.0294	6.12	19.97	7.2	63.7	5.6
KAHO-NHP well. 2	10/29/12	4161-02	19.6858	−156.0236	4.93	20.93	7.6	72.7	6.3
KAHO-NHP well 3	10/29/12	4061-01	19.6783	−156.0222	11.09	21.07	6.8	58.9	4.9
seawater	10/26/12	n/a	19.6684	−156.0320	35.4	27.2	n/a	n/a	n/a

2.2. Honokōhau Harbor transect

To quantify the size and shape of the SGD plume, a shore-perpendicular transect was sampled within and offshore of the Honokōhau Harbor for temperature and salinity (Fig. 1c). Using a small boat and a calibrated SONTEK CastAway handheld CTD (sampling rate = 5 Hz), 18 vertical profiles of water column temperature and salinity were made along a 1.4-km transect to the interior terminus of the harbor (Fig. 1c). The Honokōhau Harbor is a small boat marina that was excavated from the coastal lava in 1970 and expanded in 1978. A persistent influx of brackish groundwater along the most eastern (inland) extent of the harbor was observed in the distributions of temperature, salinity, and nutrient anomalies (Bienfang, 1980; Parsons et al., 2008).

2.3. Endmember samples

Groundwater endmember samples were collected in October 2012 during low tide and a relatively dry period from three shallow groundwater observation wells located within the northern half of Kaloko-Honokōhau NHP (state well numbers 4061-01, 4161-02, and 4161-01), a lava tube near Kīholo Bay approximately 23 km north of the Honokōhau Harbor, and the Honokōhau Harbor (HH) monitor well no. 2 located just downstream (550 m) from the Kealakehe effluent disposal site and upslope of the southern end of the Park (Fig. 1). For comparison, effluent from the Kealakehe WWTF was also collected in October 2012 for analyses. All but the lava tube sampling sites were drilled and cased with PVC and frequently sampled. An YSI multi-sensor probe was used to monitor temperature, pH, and dissolved oxygen (% and mg l^{-1}) from the sampling wells (Table 1). In-situ salinities from the wells within the Park range from 4.93 to 11.09 (Table 1), characteristic of the Park's groundwater flow system that is composed of brackish water overlying saltwater (Oki et al., 1999). Salinity from the HH monitor well no. 2 was 5.7, whereas groundwater collected from the lava tube was fresher, measured at 2.0. Using a Fultz Pump, groundwater was collected after purging the wells by pumping at least three well volumes at a flow rate of approximately 4 L min^{-1}. Five-liter water samples were collected in acid-washed carboys and kept chilled for sequential filtration, as described in detail below. A 40-L surface seawater sample was collected 500 m seaward from the mouth of the harbor (Fig. 1), and is considered representative of the seawater endmember. The location where the surface seawater sample was collected is also characterized by extensive coral growth (Cochran et al., 2006). Water collected from the HH monitor well no. 2 and lava tube sampling sites was mixed with local ocean seawater (salinity 35.4) to construct salinity gradients as described below.

2.4. Mixing experiment and sequential filtration

Two sets of mixing experiments were conducted by combining aliquots of the representative groundwater endmembers collected either from the HH monitor well no. 2 or the lava tube site, with aliquots of the local seawater endmember to construct a full salinity gradient. Resultant mixtures of known salinities were allowed to equilibrate for a minimum of 2 h to ensure sufficient mixing between endmembers. Once thoroughly mixed, sequential filtration was conducted to examine the potential role of colloids on trace element concentrations (Sholkovitz, 1995). Using a peristaltic pump and a 0.45-μm Geotech in-line filter, a mixed water sample was first filtered to obtain a colloid fraction (0.02–0.45 μm). To separate the colloid fraction from the "truly dissolved" fraction (<0.02 μm) for trace elements, the sample was then further filtered through a 0.02-μm syringe filter. In contrast, only the colloid fraction was collected for nutrient analysis using a 0.45-μm Geotech in-line filter. All samples were collected into acid-washed polyethylene sample bottles and stored frozen. A replicate nutrient sample for PO_4^{3-} analysis was collected and acidified to pH < 2 with ultra-pure 6 N nitric acid following previously established protocols to prevent scavenging by precipitation of iron oxides (Swarzenski et al., 2007). Suspended particulate matter (SPM) concentrations were also obtained from separate 1-L water samples that were filtered through pre-weighed 0.45 μm glass fiber filters (GFF).

(b) observation well sites in the Kaloko-Honokōhau National Historical Park (KAHO-NHP; green boundary) and seawater sampling site (white star) in Kaloko Bay. Honokōhau Harbor monitor well no. 2 (HH), and Kealakehe wastewater treatment facility (WWTF). (c) Sampling CTD transect within Honokōhau Harbor (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

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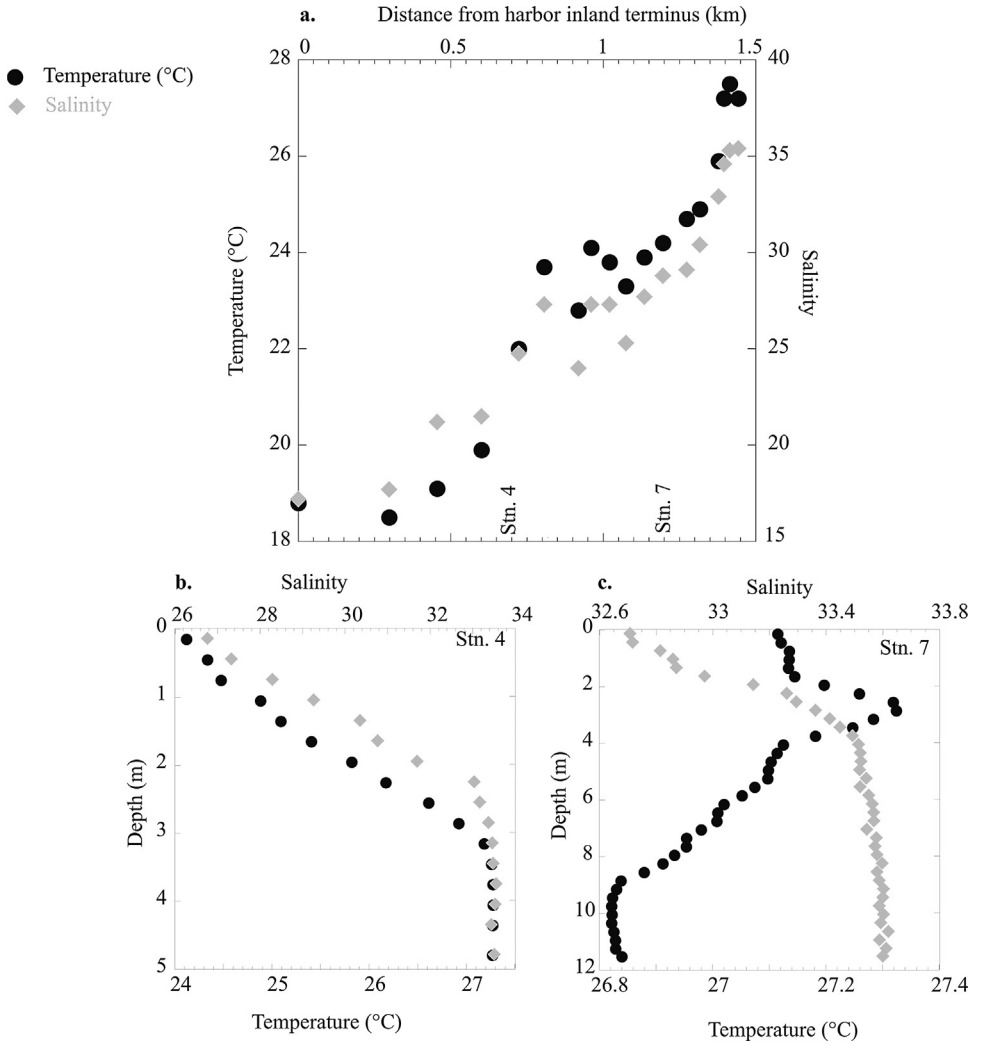

Fig. 2. (a) Plot of a ~1.5-km-long temperature and salinity transect with 18 stations across the Honokōhau Harbor created from high-resolution vertical profiles of water column temperature and salinity. Vertical profiles for CTD stations (b) no. 4 and (c) no. 7 sampled at 0.7 and 1.2 km from the harbor inland terminus, respectively.

2.5. Nutrient and trace element analyses

Nutrients were analyzed at the Woods Hole Oceanographic Institution (WHOI) via flow injection analysis for ammonium (NH_4^+), silicic acid (H_4SiO_4), phosphate (PO_4^{3-}), and nitrate + nitrite ($NO_3^- + NO_2^-$) with precisions of 0.60%, 0.78%, 0.86%, and 0.33% relative standard deviation, respectively. Total dissolved nitrogen (TDN) was measured by persulfate oxidation, dissolved inorganic nitrogen (DIN) was calculated as $NH_4^+ + NO_2^- + NO_3^-$, and dissolved organic nitrogen (DON) was calculated as TDN-DIN. The nutrient analyses for the Kealakehe WWTF sample were done by the SOEST Lab for Analytical Biogeochemistry (SLAB) at the University of Hawaii at Manoa. TDN was measured using persulfate oxidation with a relative standard deviation of 0.98%. DIN and DON concentrations we calculated as above. A suite of trace elements with sensitivity to both SGD and land based-sources were determined by high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) at the University of Southern Mississippi. Select trace element (Mo, Ba, Re, V, and U) concentrations with detection limits above background are reported below.

3. Results

3.1. Harbor CTD transect and in-situ mixing

The general trend in water properties (i.e., temperature and salinity) from a cross-shore transect conducted within and offshore of the Honokōhau Harbor is a freshening and cooling of surface water toward the harbor inland terminus (Fig. 2).

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Table 2a
Trace element concentration (nM) for groundwater (GW) end members collected from the Kona Coast, Hawai'i from the colloid bound (0.02–0.45 μm) and truly dissolved (<0.02 μm fractions isolated through sequential filtration.

Element	HH monitor well no. 2		Lava tube, Kiholo Bay		KAHO-NHP well 1		KAHO-NHP well 2		KAHO-NHP well 3	
[nM]	0.45 μm	0.02 μm	0.45 μm	0.02 μm	0.45 μm	0.02 μm	0.45 μm	0.02 μm	0.45 μm	0.02 μm
Mo	29	31	66	66	36	37	30	30	50	49
Ba	45	45	43	40	27	27	21	21	44	43
V	744	698	2150	2176	1750	1669	1247	1673	1079	1151
U	<1	<1	2	2	3	3	2	2	4	4

Table 2b
Trace element concentration (nM) for local nearshore seawater end members collected from the Kona Coast, Hawai'i from the colloid bound (0.02–0.45 μm) and truly dissolved (<0.02 μm) fractions isolated through sequential filtration.

Element	Seawater transect 1		Seawater transect 2	
[nM]	0.45 μm	0.02 μm	0.45 μm	0.02 μm
Mo	112	210	112	113
Ba	35	45	36	35
V	68	49	72	58
U	12	9	12	11

Table 3
Nutrient concentration reported as mean and standard deviation (±) in μM for ammonium (NH_4^+), silicate (SiO_2^-), phosphate (PO_4^-), and nitrate + nitrite ($NO_3^- + NO_2^-$) with precision of 0.6%, 0.78%, 0.86% and 0.33% relative standard deviation. *Samples acidified after filtration.

Site	PO_4^{3-} (μM)	PO_4^{3-} (μM)*	H_4SiO_4 (μM)	NH_4^+(μM)	$NO_2^- + NO_3^-$ (μM)	TDN (μM)	DON (μM)
HH monitor well no. 2	26.2	37.3	376.2	1.3	187.4	255.2	66.6
Lava tube, Kiholo Bay	1.9	2.1	432	0.3	26.5	27.7	1.0
KAHO-NHP well 1	3.6	4.1	389.1	0.9	66.5	69.1	66.5
KAHO-NHP well 2	2.1	2.3	392.1	1.1	31.2	52.6	31.2
KAHO-NHP well 3	2.7	3.0	310.7	2.2	39.3	50.7	39.3
Kealakehe WWTF	220.3	n/a	890.4	1.7	860.2	n/a	n/a
Local seawater	0.1	0.4	28.4	0.1	4.1	21.6	17.3

A shift in the pattern of temperature and salinity vertical profiles was observed at CTD station no. 7 (Fig. 2c), approximately 1.2 km from the harbor inland terminus, where temperatures decreased with depth below 4 m (Fig. 2b). Oceanic conditions in temperature and salinity were reached at a distance of 1.5 km seaward from the harbor back wall. Salinity and temperature increase in a steady and generally linear fashion with distance from the harbor terminus with deviations from the mixing line observed at salinities less than 25 (Fig. 2a)

3.2. Trace elements and experimental mixing

Trace element concentrations in the colloid fraction (0.02–0.45 μm) were statistically indistinct (Student *T*-test; $p > 0.05$) from the truly dissolved (<0.02 μm) fraction in the groundwater endmembers (Tables 2a and b). Mean vanadium (V) concentrations were highest (2176 nM) in the groundwater endmember collected from the nearshore lava tube, whereas local seawater endmember V concentrations ranged between 49 and 71 nM. Barium (Ba) also exhibited enrichment in the groundwater endmember samples with similar concentrations at the HH monitor well no. 2 and lava tube sampling sites, ranging from 40 to 45 nM (Table 2a). In contrast, Mo and U concentrations were higher at marine salinities (Fig. 3). Enrichment was observed for U and V at the lava tube and the Park sampling sites relative to the HH monitor well no. 2 site (Table 2). Trace element-salinity relations are illustrated in Fig. 3 and are generally conservative. Mixing lines for Ba and V are inverse with salinity, whereas Mo, and U are positively correlated to salinity (Fig. 3).

3.3. Nutrients and experimental mixing

Nutrient concentrations (H_4SiO_4, PO_4^{3-}, and NO_3^-, and NO_2^-) in the coastal groundwater endmembers were enriched relative to seawater concentrations with the exception of NH_4^+ for which overall concentrations were negligible (<2 μM) (Table 3). Expectedly, the WWTF sample was the most nutrient enriched. PO_4^{3-} and $NO_2^- + NO_3^-$ concentrations were enriched in the HH monitor well no. 2 site relative to the other groundwater sampling sites (Table 3). Elevated nitrogen concentrations at this site were dominated by NO_3^- rather than NO_2^-. The enrichment at the HH monitor well no. 2 site was also observed in TDN, DON, and DIN values, with TDN values dominated by inorganic N (Table 3).

Nutrient concentrations from this study display a conservative inverse relation with salinity (Table 4; Fig. 4). The exception to this pattern is PO_4^{3-} from the HH monitor well no. 2 mixing experiment, where pronounced deviations from the conservative mixing line are observed in both the acidified and unacidified samples (Fig. 5). Instead of a linear mixing line, the

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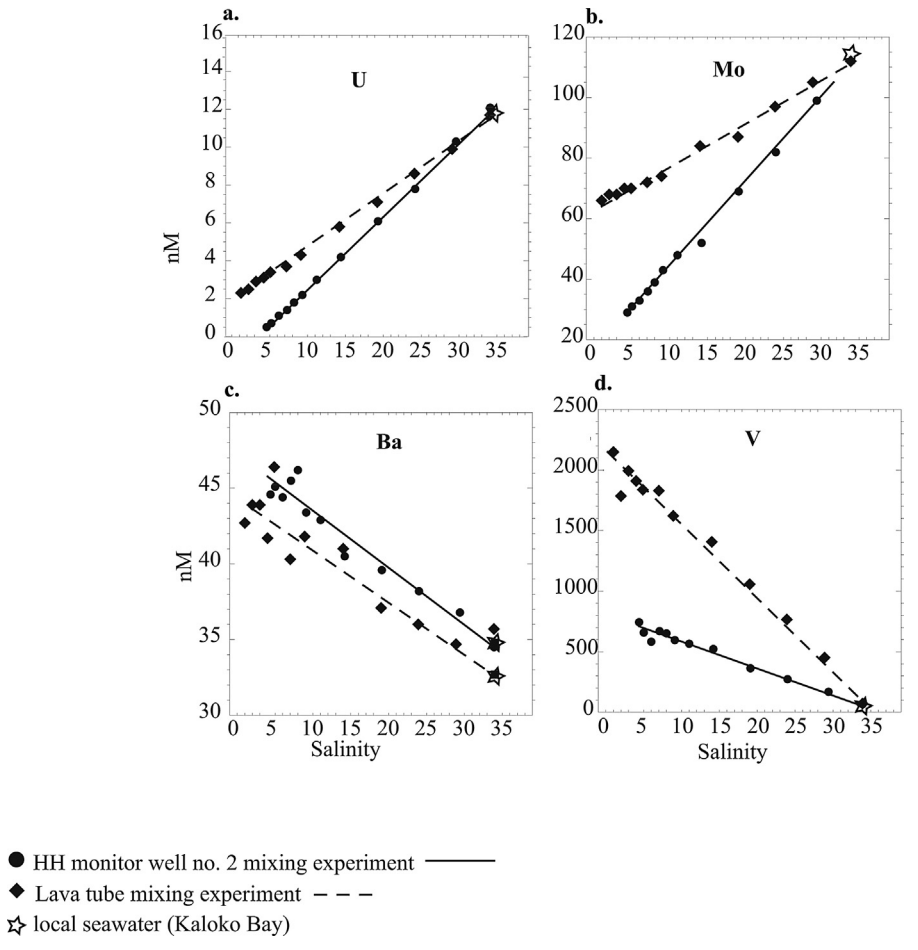

Fig. 3. Experimental mixing gradients for the colloid fraction of select trace elements from groundwater endmembers collected from Honokōhau Harbor (HH) monitor well no. 2 (circles; solid line) and a lava tube near Kīholo Bay (squares; dashed line) mixed with local seawater for (a) uranium (U), (b) molybdenum (Mo), (c) barium (Ba), and (d) vanadium (V) in nM. Trace element concentrations for local seawater (stars). The best-fit regression line is shown for the experimental mixing lines for each trace element. For comparison, low salinity (<1) U concentrations from the regional coastal unconfined groundwater (freshwater-lens system) ranged from at 0.28 to 0.69 nM (Tillman et al., 2014).

Table 4
Equations for two endmember mixing model constructed from experimental mixing of local seawater and groundwater from the Honokohau Harbor (HH) monitor well no. 2 and groundwater from a lava tube in the relatively rural Kiholo Bay region. Mixing lines are reported for (nutrients (μM), trace elements (nM), pH, and suspended particulate matter (SPM, mg L^{-1}) with respective correlation coefficients ($p \leq 0.05$). *Samples acidified after filtration.

Parameter	HH monitor well no.2	correlation coefficient	Lavatube, Kiholo Bay	correlation coefficient
H_4SiO_4 (μM)	$y = -11.41x + 462.43$	$R^2 = 0.97$	$y = -10.41x + 428.28$	$R^2 = 0.93$
PO_4^{3-} (μM)	$y = -0.11x^2 + 3.49x + 9.03$	$R^2 = 0.99$	$y = -0.06x + 1.92$	$R^2 = 0.78$
PO_4^{3-} (μM)*	$y = -0.08 \times^2 + 2.23x + 26.74$	$R^2 = 0.99$	$y = -0.07x + 2.53$	$R^2 = 0.95$
$NO_2^- + NO_3^-$ (μM)	$y = -6.23x + 237.67$	$R^2 = 0.97$	$y = -0.98x + 39.93$	$R^2 = 0.64$
Mo (nM)	$y = 2.79x + 13.36$	$R^2 = 0.99$	$y = 1.39x + 62.39$	$R^2 = 0.99$
Ba (nM)	$y = -0.37x + 47.44$	$R^2 = 0.94$	$y = -0.30x + 44.49$	$R^2 = 0.81$
V (nM)	$y = -21.42x + 816.29$	$R^2 = 0.98$	$y = -58.66x + 2200.70$	$R^2 = 0.98$
U (nM)	$y = 0.39x - 1.71$	$R^2 = 0.99$	$y = 0.28x + 1.64$	$R^2 = 0.99$
pH	$y = 0.02x + 7.42$	$R^2 = 0.80$	$y = 0.01x + 7.83$	$R^2 = 0.23$
SPM mg L^{-1}	$y = 3.82x + 1.02$	$R^2 = 0.75$	$y = 3.45x - 0.563$	$R^2 = 0.94$

phosphate data can be fit with a polynomial equation ($R^2 = 0.98–0.99$), with the acidified and unacidified phosphate mixing curves merging at a salinity > 20 (Fig. 5a). Phosphate values peak at a salinity of 15, with peak values 3.8 and 10.6 μM greater than the HH monitor well no. 2 endmember for the acidified and unacidified mixing experiments, respectively. As a result, there is a net release of PO_4^{3-} of 463 μM and 372 μM for the unacidified and acidified mixing experiments, respectively (Fig. 5a).

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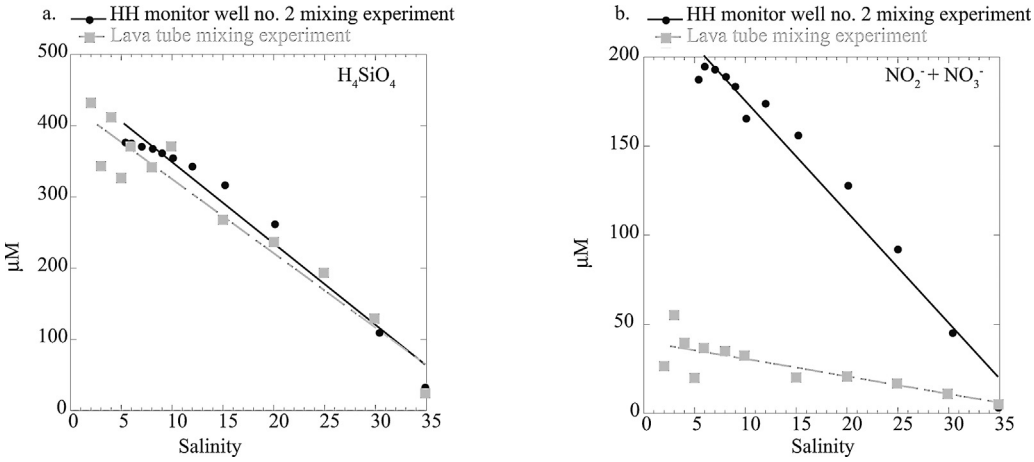

Fig. 4. Experimental mixing lines for the colloid fraction for (a) silicic acid (H_4SiO_4) and (b) nitrate + nitrite ($NO_3^- + NO_2^-$) from groundwater endmembers collected from Honokōhau Harbor (HH) monitor well no. 2 (circles, dashed line) and a lava tube near Kīholo Bay (squares, solid line) mixed with local seawater.

4. Discussion

4.1. Source waters

Previous work along the Kona coast demonstrates the conservative behavior of nutrients as a result of mixing between fresh, high-nutrient groundwater and saline, low-nutrient seawater (Parsons et al., 2008; Street et al., 2008; Peterson et al., 2009; Knee et al., 2010). Overall, nutrient concentrations at higher salinities are close to seawater levels, reflecting the effectiveness of physical mixing on nearshore nutrient concentrations (Bienfang et al., 2009). Results from our mixing experiments are in agreement with previous observations along the Kona coast (Johnson et al., 2008; Knee et al., 2010), where elevated nutrient concentrations are attributed to weathering of lava substrate and organic matter, and anthropogenic sources including fertilizers and septic leachate (Hunt, 2014). As such, the geochemical characteriztics of the freshwater endmembers are important as are the processes (physical, chemical, and biological) occurring during transport. Elevated nutrient concentrations at the HH sampling well no. 2 relative to the observation wells within the Park and the Kīholo lava tube are likely a reflection of proximity to the Kealakehe WWTF (Johnson et al., 2008).

Relative to WWTF endmember nutrient concentrations, the SGD endmember concentrations from the HH monitor well no. 2 is a mixture of WWTF effluent that has undergone dilution from mixing with groundwater and seawater, consistent with coastal aquifer mixing processes (Bienfang, 1980). The comparatively lower total *N* and *P* values within the Park and lava tube sampling site reflect the fact that these sites are not directly downstream of point-source pollution. However, elevated nutrients, particularly N and P in the HH monitor well no. 2 indicate an anthropogenic source at this site (Bienfang and Johnson, 1980; Johnson et al., 2008; Knee et al., 2010; Hunt 2014).

Although the WWTF appeared to be a point source of nutrients, that was not true of trace elements. Elements with a distinct terrestrial source include Ba and V. Given the enrichment of both elements in basalt, and the significant V enrichment in the lava tube endmember, Ba and V are most likely sourced from weathering of relatively young volcanic rocks of the parent basaltic aquifer of the Hualālai Volcano (De Carlo et al., 2004; De Carlo et al., 2005). In particular, V concentrations from the Kaupulehu flow, which is located where the lava tube sample was taken, are particularly high (Clague et al., 1980). In comparison, U and Mo were marine-sourced as is commonly reported for Mo in surface estuaries (e.g., Strady et al., 2009). Results presented here are within the range reported for a similar suite of trace elements from groundwater and surface seawater samples collected from Maui (Kahekili) and O'ahu (Niu and Black Point) (Swarzenski et al., 2013), as well as from wells on the Island of Hawai'i (Kona) (Bienfang et al., 2009).

4.2. Mixing model

The effectiveness of physical mixing on restoring nearshore trace element concentrations to oceanic levels has been observed previously (Migon et al., 2007; Bienfang et al., 2009) and is clearly evident in the two endmember mixing models for the trace elements (Fig. 3). Concentrations from the colloid and truly dissolved fractions were similar, suggesting that terrestrial particulates are not the primary carrier. This interpretation is consistent with relatively lower suspended particulate matter (>0.45 µm) concentrations in the groundwater endmember samples (Fig. 6), confirming that land-derived material flux of particulates was not conveyed by SGD at least during this sampling period. Therefore, the conservative nature of the SGD-sourced trace elements, Ba and V, indicate that dilution is the main driver of dissolved trace element concentrations.

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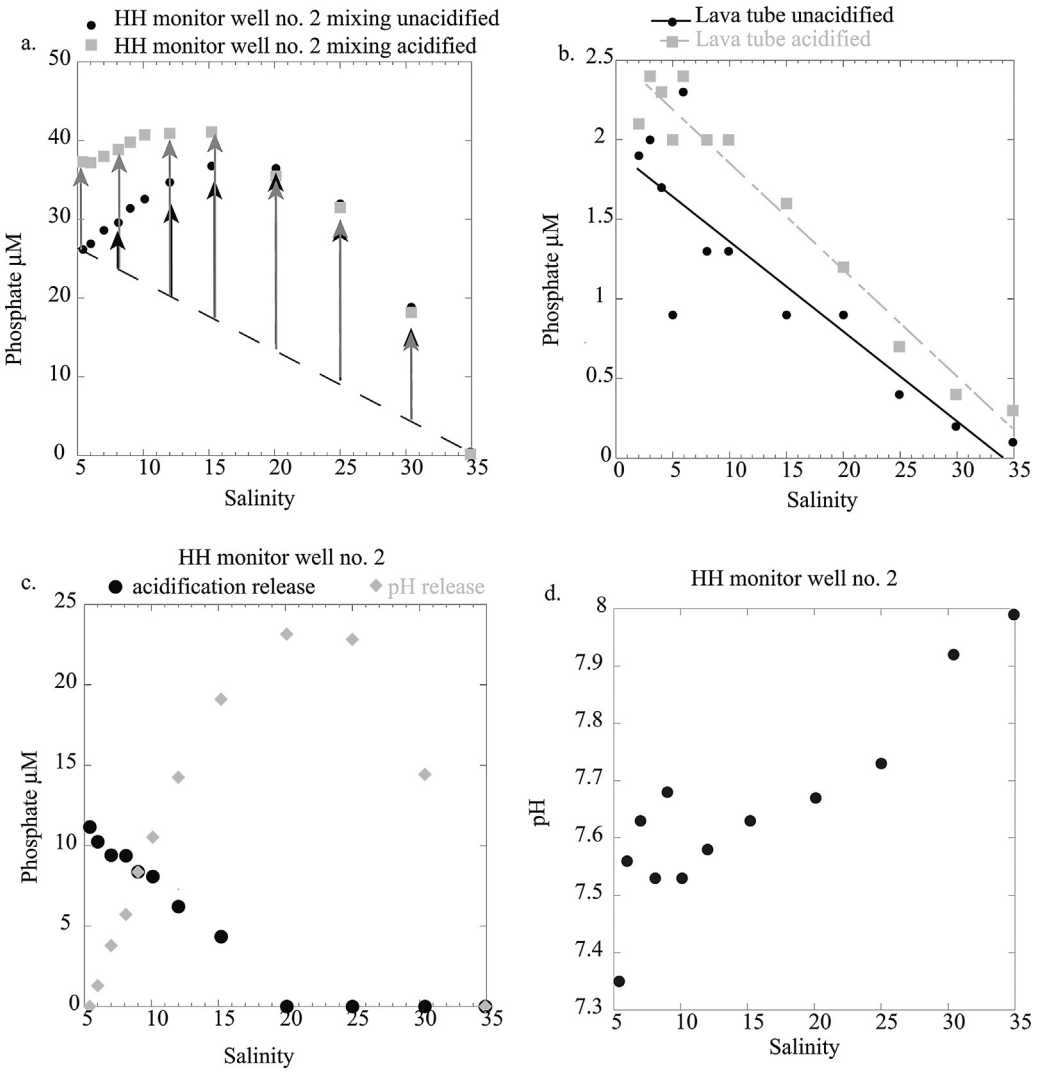

Fig. 5. Experimental mixing lines for the colloid fraction for phosphate from groundwater endmembers collected from the (a) Honokōhau Harbor (HH) monitor well no. 2 and (b) lava tube near Kīholo Bay mixed with local seawater for both acidified (square) and unacidified (circle) samples. Net release of phosphate from the Honokōhau Harbor (HH) monitor well no. 2 mixing experiments are indicated with arrows for the acidified (grey) and unacidified (black) samples. (c) Release of phosphate (10 µM) from the Honokōhau Harbor (HH) monitor well no. 2 mixing experiment due to acidification and changes in seawater pH. (d) Increase in pH relative to salinity from the Honokōhau Harbor monitor well no. 2 mixing experiment.

The importance of dilution by mixing is also apparent in the experimental mixing model results for nutrients. In the absence of biological processes (e.g., nitrification), the $H_4SiO_4^-$ and NO_3^- mixing lines are strictly a manifestation of a two-endmember mixing model, controlled by input from the basaltic aquifer for H_4SiO_4, and land-based activities (e.g., treated wastewater and fertilizer) contributing to increased N-loading (Knee et al., 2010). In contrast, the non-conservative behavior of PO_4^{3-} suggests that changes in surface complexation are controlling PO_4^{3-} concentrations. Results from our experimental mixing model indicate changes in colloid sorption capacity exert a greater control over PO_4^{3-} behavior relative to the effects of dilution. The strong sorption capacity of iron oxyhydroxides for group 5 elements, particularly phosphate and arsenate, have been demonstrated in both lab and field studies (e.g., Gao and Mucci, 2001; Gao and Mucci, 2003; Chitrakar et al., 2006; Spiteri et al., 2008). Release of colloid bound P has been referred to as the "iron conveyor belt" by (Jordan et al., 2008), where release of PO_4^{3-} is due to decreased adsorption of PO_4^{3-} from metal oxyhydroxides by changing the charge of the adsorbent. Release of PO_4^{3-} appears to be triggered by both directly acidifying the sample to release total dissolved phosphorus, and subsequent mixing with seawater of higher pH to release the soluble reactive phosphorus. Acidification of the sample triggered the initial release of PO_4^{3-}, releasing approximately 10 µM (Fig. 5c). However, at salinity values > 10 the effect of acidifying on PO_4^{3-} release decreases and the exponential increase in PO_4^{3-} appears to be related to a change in seawater pH (Fig. 5c). As reported above, there is a net release of PO_4^{3-} of 463 µM over the full salinity gradient from the

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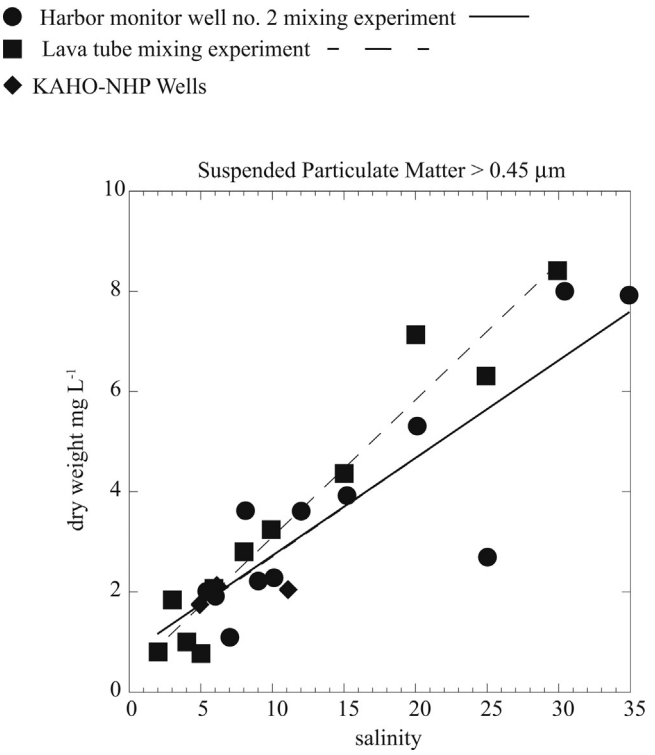

Fig. 6. Suspended particulate matter (SPM; dry weight mg L^{-1}) versus salinity for the experimental mixing from groundwater endmembers collected from the Honokōhau Harbor monitor well no. 2 (circles), and lava tube near Kīholo Bay (squares) mixed with local seawater, as well as SPM concentration from observation wells within Kaloko-Honokōhau National Historical Park (KAHO-NHP) (diamonds).

unacidified samples. Multiplying this net release by the fresh SGD flux (210–310 L m^{-1} min^{-1}; Knee et al., 2010) suggests that 140–206 mol m^{-1} day^{-1} of soluble reactive phosphorus could be released from groundwater upon mixing with seawater over the full salinity gradient.

The effect of pH on adsorption of phosphate has been previously observed in seawater for goethite precipitate (FeO(OH)), where maximum adsorption occurs at a pH of 7 (e.g., (Gao and Mucci, 2003). At higher pH values adsorption decreases due to electrostatic repulsion of phosphate as the hydroxide becomes more negative at higher pH (Chitrakar et al., 2006). The range and increase of pH values relative to salinity (Fig. 5d) supports the notion that a pH-driven change in the surface charge of oxyhydroxides is most likely driving the release of PO_4^{3-} into solution over the observed salinity gradient. To a lesser degree, desorption of H_4SiO_4 in the mid salinity range in the HH monitor well no. 2 mixing experiment (Fig. 4a) can also be explained by surface complexation effects given the affinity of aqueous silica to sorb to the surfaces of oxides (e.g., Davis et al., 2002).

As described earlier, peak PO_4^{3-} values from the HH monitor well no. 2 mixing experiment occur at a salinity of 15 (Fig. 5a). Spiteri et al. (2008) found that at a salinity of 15 the molar ratio of total dissolved plus adsorbed phosphate to total surface binding site concentrations was the greatest. Spiteri et al. (2008) conclude that the rapid decrease in SPM and subsequent drop in available binding sites can explain the non-conservative PO_4^{3-} behavior. Whereas the non-conservative behavior of phosphate in estuaries is generally attributed to desorbing from soil and sediment particles, results from our current study demonstrate that in a subterranean estuary desorption from colloids may play an important role in PO_4^{3-} behavior. The release of oxyhydroxide-bound phosphate within the groundwater-seawater mixing zone must therefore be taken into account in terms of total delivery of phosphorous to the ocean. Results from our mixing experiments demonstrate how relative availability of phosphorous can shift with adsorption behavior, substantially affecting the mobility of phosphate in the FW-SW mixing zone, as well as potential interactive effects with trace metals. For example, high concentrations of PO_4^{3-} can enhance the mobility of arsenic in water through competition for adsorption sites (Smedley and Kinniburgh, 2002), and alter biological uptake of metals in aquatic organisms (e.g., Riedel et al., 2003). Likewise, Miao and Wang (2006) found nutrient addition strongly influenced uptake of Cd in marine diatom species, similar to findings of Wang and Dei (2001). Confirmation of these processes requires a more comprehensive study by ideally combining results from this laboratory study with field studies.

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5. Conclusion

In contrast to conventional estuarine mixing where rivers supply terrestrial material to coastal waters, persistent discharge of groundwater to coastal waters along the Kona coast of Hawai'i supplies the majority of nutrients and select trace elements. Results presented here indicate conservative mixing of trace elements with salinity based on two distinct mixing models with groundwater endmembers from a lava tube site downstream of a relatively rural region, and an impacted well site downstream from a WWTF. The WWTF-treated effluent was the main source for nutrient enrichment of groundwater near the Honokōhau Harbor and in the mixing zone. Dilution from physical mixing can reduce the impact of land-derived nutrient and trace element to the nearshore environment. However, the non-conservative behavior of phosphate represents an important reservoir of bio-available phosphorous in excess of that dissolved in groundwater. Results from this study provide additional insights into the patterns and processes that influence the fate of SGD mixing with nearshore waters, which can ultimately impact the nearshore water quality of coral ecosystems. With phosphorous commonly a bio-limiting nutrient, readily incorporated in soft tissues of marine organisms, and a major nutrient contributing to eutrophication, the shifting availability of phosphorous can potentially make prioritizing nutrient management more complex.

Conflict of interest

None.

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References

Anderson, D.M., Glibert, P.M., Burkholder, J.M., 2002. Harmful algal blooms and eutrophication: nutrient sources, composition and consequences. Estuaries 25, 562–584.
Andrefouet, S., Mumby, P.J., McField, M., Hu, C., Muller-Karger, F.E., 2002. Revisiting coral reef connectivity. Coral Reefs 21, 43–48.
Basu, A.R., Jacobsen, S.B., Poreda, R.J., Dowling, C.B., Aggarwal, P.K., 2001. Large groundwater strontium flux to the oceans from the Bengal Basin and the marine strontium iIsotope record. Science 293, 1470–1473.
Bauer, G., 2003. A Study of the Ground-Water Conditions in North and South Kona and South Kohala Districts Island of Hawaii, 1991–2002 Commission on Water Resource Management PR-2003-01. Department of Land and Natural Resources, Honolulu, Hawaii, 95p.
Beck, A.J., Cochran, M.A., 2013. Controls on solid-solution partitioning of radium in saturated marine sands. Mar. Chem. 156, 38–48.
Beck, A.J., Tsukamoto, Y., Tovar-Sanchez, A., Huerta-Diaz, M., Bokuniewicz, H.J., Sañudo-Wilhelmy, S.A., 2007. Importance of geochemical transformations in determining submarine groundwater discharge-derived trace metal and nutrient fluxes. Appl. Geochem. 22, 477–490.
Bienfang, P., 1980. Water quality characteristics of Honokohau Harbor: a subtropical embayment affected by groundwater intrusion. Pac. Sci. 34, 279–291.
Bienfang, P., De Carlo, E.H., Christopher, S., DeFelice, S., Moeller, P., 2009. Trace element concentrations in Coastal Hawaiian waters. Mar. Chem. 113, 164–171.
Bone, S.E., Charette, M.A., Lamborg, C.H., Gonneea, M.E., 2007. Has submarine groundwater discharge been overlooked as a source of mercury to coastal waters? Environ. Sci. Technol. 41, 3090–3095.
Bruno, J.F., Petes, L.E., Harvell, C.D., Hettinger, A., 2003. Nutrient enrichment can increase the severity of coral diseases. Ecol. Lett. 6, 1056–1061.
Chitrakar, R., Tezuka, S., Sonoda, A., Sakane, K., Ooi, K., Hirotsu, T., 2006. Phosphate adsorption on synthetic goethite and akaganeite. J. Colloid Interface Sci. 298, 602–608.
Clague, D., Jackson, E., Wright, T., 1980. Petrology of Hualalai Volcano, Hawaii: implication for mantle composition. In: Garcia, M.O., Decker, R., (Eds.) Bulletin Volcanologique, GA Macdonald Special Memorial Issue, pp. 641–656.
Clague, D.A., 1987. Hawaiian Alkaline Volcanism, in Alkaline Igneous Rocks. In: Fitton, J.G., Upton, B.G.J. (Eds.). Geological Society Special Publication, pp. 227–252.
Cochran, S., Gibbs, A., Logan, J., 2006. Benthic Habitat Maps for National Parks along the Kona Coast Hawai"i. In Eos. Trans. AGU 87(36), Ocean Sciences Meeting Supplement, CD-rom, Abstract OS26I-02.
Davis, C.C., Chen, H.-W., Edwards, M., 2002. Modeling silica sorption to iron hydroxide. Environ. Sci. Technol. 36, 582–587.
De Carlo, E.H., Beltran, V.L., Tomlinson, M.S., 2004. Composition of water and suspended sediment in streams of urbanized subtropical watersheds in Hawaii. Appl. Geochem. 19, 1011–1037.
De Carlo, E.H., Tomlinson, M.S., Anthony, S.A., 2005. Trace elements in streambed sediments of small subtropical streams on Oahu, Hawaii: results from the USGS NAWQA program. Appl. Geochem. 20, 2157–2188.
Fabricius, K.E., 2005. Effects of terrestrial runoff on the ecology of corals and coral reefs: review and synthesis. Mar. Pollut. Bull. 50, 125–146.
Gao, Y., Mucci, A., 2001. Acid base reactions, phosphate and arsenate complexation, and their competitive adsorption at the surface of goethite in 0.7 M NaCl solution. Geochim. Cosmochim. Acta 65, 2361–2378.
Gao, Y., Mucci, A., 2003. Individual and competitive adsorption of phosphate and arsenate on goethite in artificial seawater. Chem. Geol. 199, 91–109.
Giambelluca, T.W., Chen, Q., Frazier, A.G., Price, J.P., Chen, Y.-L., Chu, P.-S., Eischeid, J.K., Delparte, D.M., 2013. Online Rainfall Atlas of Hawai,i. Bull. Amer. Meteor. Soc. 94, 313–316.
Gingerich, S.B., Oki, D.S., 2000. Ground Water in Hawaii. U.S. Geological Survey Fact Sheet, pp. 126–1260.
Gonneea, M.E., Mulligan, A.E., Charette, M.A., 2013. Seasonal cycles in radium and barium within a subterranean estuary: implications for groundwater derived chemical fluxes to surface waters. Geochim. Cosmochim. Acta 119, 164–177.

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Howarth, R., Anderson, D., Cloern, J., Elfring, C., Hopkinson, C., Lapointe, B., Malone, T., Marcus, N., McGlathery, K., Sharpley, A., Walker, D., 2000. Nutrient pollution of coastal rivers, bays, and seas. Issues Ecol. 7, 1–15.
Hughes, T.P., Rodrigues, M.J., Bellwood, D.R., Ceccarelli, D., Hoegh-Guldberg, O., McCook, L., Moltschaniwskyj, N., Pratchett, M.S., Steneck, R.S., Willis, B., 2007. Phase shifts, serbivory, and the resilience of coral reefs to climate change. Curr. Biol. 17, 360–365.
Hunt, C.D, Jr., 2014. Baseline water-quality sampling to infer nutrient and contaminant sources at Kaloko-Honokōhau National Historical Park, Island of Hawai'i, 2009 US Geological Survey Scientific Investigations Report 2014-5158, 52.
Johnson, A.G., Glenn, C.R., Burnett, W.C., Peterson, R.N., Lucey, P.G., 2008. Areal infrared imaging reveals large nutrient-rich groundwater inputs to the ocean. Geophys. Res. Lett. 35, 1–6.
Jordan, T.E., Cornwell, J.C., Boynton, W.R., Anderson, J.T., 2008. Changes in phosphorus biogeochemistry along an estuarine salinity gradient: the iron conveyer belt. Limnol. Oceanogr. 53, 172–184.
Knee, K., Street, J., Grossman, E., Boehm, A., Paytan, A., 2010. Nutrient inputs to the coastal ocean from submarine groundwater discharge in a groundwater-dominated system: relation to land use (Kona coast, Hawaii, U.S.A.). Limnol. Oceanogr. 55, 1105–1122.
Langenheim, V.A.M., Clague, D.A., 2015. The Hawaiiian-emperor volcanic chain. Part II. Stratigraphic framework of volcanic rocks of the Hawaiian islands. In: Decker, R.W., Wright, T.L., Stauffer, P.H. (Eds.), Volcanism in Hawaii, 1350. U.S. Geological Survey Professional Paper, pp. 55–84.
Lapointe, B.E., Barile, P.J., Littler, M.M., Littler, D.S., 2005. Macroalgal blooms on southeast Florida coral reefs. II. Cross-shelf δ^{15}N values provide evidence of widespread sewage enrichment. Harmful Algae 4, 1106–1122.
Miao, A.-J., Wang, W.-X., 2006. Cadmium toxicity to two marine phytoplankton under different nutrient conditions. Aquat. Toxicol. 78, 114–126.
Migon, C., Ouillon, S., Mari, X., Nicolas, E., 2007. Geochemical and hydrodynamic constraints on the distribution of trace metal concentrations in the lagoon of Noumeía, New Caledonia. Estuar. Coast Shelf Sci. 74, 756–765.
Moore, W.S., 1996. Large groundwater inputs to coastal waters revealed by ^{226}Ra enrichments. Nature 380, 612–614.
Moore, W.S., 2010. The fffect of submarine groundwater discharge on the ocean. Annu. Rev. Mar. Sci. 2, 59–88.
Moore, W.S., Blanton, J.O., Joye, S.B., 2006. Estimates of flushing times, submarine groundwater discharge, and nutrient fluxes to Okatee Estuary, South Carolina. J. Geophys. Res.: Oceans 111, C09006.
Oki, D.S., 1999. Geohydrology and numerical simulation of the ground-water flow system of Kona, Hawaii US Geological Survey Water-Resources Investigations Report 99-4073 70p.
Oki, D.S., Tribble, G.W., Souza, W.R., Bolke, E.L., 1999. Groundwater resources in Kaloko-Honokōhau National Historic Park, island of Hawai'i, and numerical simulation of the effects of groundwater withdrawals US Geological Survey Water Resources Investigations Report 99-4070 49 p.
Parsons, M.L., Walsh, W.J., Settlemier, C.J., White, D.J., Ballauer, J.M., Ayotte, P.M., Osada, K.M., Carman, B., 2008. A multivariate assessment of the coral ecosystem health of two embayments on the lee of the island of Hawai'i. Mar. Pollut. Bull. 56, 1138–1149.
Peterson, R.N., Burnett, W.C., Glenn, C.R., Johnson, A.G., 2009. Quantification of point-source groundwater discharges from the shoreline of the Big Island, Hawai. Limnol. Oceanogr. 54, 890–904.
Redding, J.E., Myers-Miller, R.L., Baker, D.M., Fogel, M., Raymundo, L.J., Kim, K., 2013. Link between sewage-derived nitrogen pollution and coral disease severity in Guam. Mar. Pollut. Bull. 73, 57–63.
Riedel, G., Sanders, J., Breitburg, D., 2003. Seasonal variability in response of estuarine phytoplankton communities to stress: linkages between toxic trace elements and nutrient enrichment. Estuaries 26, 323–338.
Santos, I.R., Burnett, W.C., Chanton, J.P., Mwashote, B., Suryaputra, I.G.N.A., Dittmar, T., 2008. Nutrient biogeochemistry in a Gulf of Mexico subterranean estuary and groundwater-derived fluxes to the coastal ocean. Limnol. Oceanogr. 53, 705–718.
Santos, I.R., Burnett, W.C., Misra, S., Suryaputra, I.G.N.A., Chanton, J.P., Dittmar, T., Peterson, R.N., Swarzenski, P.W., 2011. Uranium and barium cycling in a salt wedge subterranean estuary: the influence of tidal pumping. Chem. Geol. 287, 114–123.
Shaw, T.J., Moore, W.S., Kloepfer, J., Sochaski, M.A., 1998. The flux of barium to the coastal waters of the southeastern USA: the importance of submarine groundwater discharge. Geochim. Cosmochim. Acta 62, 3047–3054.
Sholkovitz, E.R., 1995. The aquatic chemistry of rare earth elements in rivers and estuaries. Aquat. Geochem. 1, 1–34.
Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behavior and distribution of arsenic in natural waters. Appl. Geochem. 17, 517–568.
Spiteri, C., Cappellen, P.V., Regnier, P., 2008. Surface complexation effects on phosphate adsorption to ferric iron oxyhydroxides along pH and salinity gradients in estuaries and coastal aquifers. Geochim. Cosmochim. Acta 72, 3431–3445.
Strady, E., Blanc, G., Schäfer, J., Coynel, A., Dabrin, A., 2009. Dissolved uranium, vanadium and molybdenum behaviours during contrasting freshwater discharges in the Gironde estuary (SW France). Estuar. Coast Shelf Sci. 83, 550–560.
Street, J., Knee, K., Grossman, E., Paytan, A., 2008. Submarine groundwater discharge and nutrient addition to the coastal zone and coral reefs of leeward Hawai'i. Mar. Chem. 109, 355–376.
Swarzenski, P.W., Izbicki, J.A., 2009. Coastal groundwater dynamics off Santa Barbara, California: combining geochemical tracers, electromagnetic seepmeters, and electrical resistivity. Estuar. Coast. Shelf Sci. 83, 77–89.
Swarzenski, P.W., Reich, C., Kroeger, K.D., Baskaran, M., 2007. Ra and Rn isotopes as natural tracers of submarine groundwater discharge in Tampa Bay, Florida. Mar. Chem. 104, 69–84.
Swarzenski, P.W., Dulaiova, H., Dailer, M.L., Glenn, C.R., Smith, C.G., Storlazzi, C.D., 2013. A geochemical and geophysical assessment of coastal groundwater discharge at select sites in Maui and O'ahu, Hawai'i. In: Wetzelhuetter, C. (Ed.), Groundwater in the Coastal Zones of Asia-Pacific. Springer, Netherlands, pp. 27–46.
Tillman, F.D., Oki, D.S., Johnson, A.G., Barber, L.B., Beisner, K.R., 2014. Investigation of geochemical indicators to evaluate the connection between inland and coastal groundwater systems near Kaloko-Honokōhau National Historical Park, Hawai'i. Appl. Geochem. 51, 278–292.
Wang, W.-X., Dei, R.C.H., 2001. Effects of major nutrient additions on metal uptake in phytoplankton. Environ. Pollut. 111, 233–240.
Wolfe, E.W., Morris, J., 1996. Geologic map of the Island of Hawaii: U.S. Geological Survey Miscellaneous Investigations Series I-2524-A, scale 1:100,000.

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